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Process for the clarification and purification of surface waters and industrial waters containing materials in suspension

Company name: Nikex Nehézipari Külkereskedelmi Vállalat, residing in Hungary.

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The present invention concerns a process for the clarification and purification of surface waters and industrial waters containing materials in suspension.

It is known that the growing needs for drinking water and industrial water are becoming increasingly difficult to meet. The underground water reserves are limited, and in most cities it is necessary to use artificially purified surface waters as tap water.

Surface water and spring water contain suspended materials of various particle sizes, the rapid and effective elimination of which is complicated and rather uncertain using the known processes. Various clarification processes using chemical products have already been applied to water purification technology.

Clarification systems with vertical or horizontal circulation generally involve the use of preliminary purification installations preceding clarification. Aluminum sulfate, iron sulfate, and similar compounds are ordinarily used as chemical clarification agents (precipitation agents or coagulation agents). These processes have the drawback that the efficacy of the precipitation agents is inadequate, since the water to be purified is still too cloudy when it exits the clarification system. In addition, the equilibrium achieved is exceedingly fragile, since the least change in the purification technique (for example the circulation rate, the water temperature, and the elimination of the sludge formed) lowers the efficacy of the clarification too much because of the material suspended in the water. Given the fact that the safety of the process is precarious, the quantity of purified water produced is always highly variable.

Thus it may be said that the known processes for the chemical purification of water do not permit the continuous production of water in desirable quantities and qualities.

The process in accordance with the invention completely eliminates the above-mentioned problems, and its application permits the purified water to have a good, stable quality not dependent on modifying the quality of the raw water or on small changes in the addition of chemical products, which permits an economical, easy, and safe operation of the purification process. In addition, the invention has the advantage of ensuring a purification capacity which, compared to the known processes, amounts to 3 to 4 times the quantity of purified water normally produced.

In accordance with the invention, the process for the clarification of surface water or industrial water containing suspended materials is characterized by the fact that the following items are added to the water to be purified (raw water): a solid, auxiliary clarification substance (accelerator) of mineral and granular nature; a polymer with a chain structure, called a "polyelectrolyte," and possibly other customary chemical products used for the purification of water, in conjunction with the fact that the purified water is recovered after having performed the usual clarification and filtration operations, wherein the solid auxiliary substance of mineral and granular nature is recovered and put back into circulation according to a cyclical process. Quartz sand with a particle size of 100-200 microns and a specific surface of 100-500 cm²/g (according to Lea-Nurse) is used as the auxiliary clarification substance with mineral, solid, and granular features.

A polymer of a degree of polymerization exceeding 500 is used as the polymer with a chain structure or polyelectrolyte, the functional groups of which have a molecular cohesion increment of 5-20 K/mol. A battery of hydraulic cyclones is advantageously used for regeneration of the solid, auxiliary substance of mineral and granular nature.

The process in accordance with the invention is based on the following points:

1. Various polyelectrolytes have been added to suspensoid systems, i.e., water containing suspended materials, and the efficacy of clarification has been examined. It has been noted that there is a threshold concentration for solid materials in such systems and that even the most effective polyelectrolyte cannot achieve clarification when the solid substance content is below this level;
2. When solid, compact materials with a reduced specific surface such as fine quartz sand are used simultaneously with the polyelectrolytes, the diluted suspensions that contain a solid-materials level below the threshold concentration can be very effectively purified, even within a short time;
3. It is also possible to improve the efficacy of clarification and reduce the quantity of the polyelectrolyte if, in addition to the latter, use is also made of other known chemical products ordinarily employed in the clarification process (coagulation agents);

4. The substance or auxiliary agent that is added to the clarification system, i.e., quartz sand, can be used in a closed circuit, whereby it is advantageously regenerated with a battery of hydraulic cyclones.

The results listed here are based on laboratory tests or industrial tests as described below:

The first series of tests was done to determine the threshold concentration. A column of turbid liquid 30 cm in height was prepared in glass cylinders of the same size and same cross-section over their entire height. Suspended mixtures of different densities were prepared by mixing clay in water, with a high degree of dispersion. The efficacy of the clarification was measured without the addition of chemical products and with the addition of products similar to polyelectrolytes. To determine the clarification levels, the method described below was used:

The clarification rate was determined according to the increasing height of the clear liquid column as a function of time in glass cylinders, wherein there was no evidence of a distinct separation of the deposited sludge phases and of the clarified liquid column. In the glass cylinders where no separation of the phases was noted, i.e., for sludges of a highly dilute concentration, the clarification rate was determined by evaporating samples taken at successive points in time and by measuring the levels of solid materials present. It is also possible to evaluate the clarification according to the transparency of the liquid column. The results obtained are indicated in the attached drawing and table 1 accompanying this drawing. According to Figure 1, curve 1 represents the clarification rate of the suspension treated with the polyelectrolyte; curve 2 represents the suspension not treated with the polyelectrolyte as a function of the density of the turbid liquid; curve 3 corresponds to curve 2, but on a scale multiplied by 10. The results obtained show in an obvious manner that the suspensions treated with the polyelectrolyte and containing 3 g/liter of solid materials climb quickly to the maximum clarification rate. If, on the other hand, the solid-materials content is reduced too much, the clarification rate falls abruptly to zero.

For a suspension treated with chemical products, it is also possible to observe a maximum clarification, but this maximum is not reached quickly and is rather flat. The two curves share a common point at which the clarification rate is zero. These results clearly show that for highly dilute suspensoid systems and consequently for the clarification of surface water and industrial water containing solid particles in suspension, the density of the turbid liquid has a threshold concentration below which no appreciable clarification is noted.

Since during the clarification of surface water it is always necessary to take into account the presence of highly dilute and extremely dispersed suspensions, treatment with the chemical products is not in itself sufficient. For such suspensions, the chemical products used, e.g., polymers with a chain structure or polyelectrolytes, are not capable of joining the particles together to form agglomerates, with

the result that these agglomerates are unable to expand in size and it cannot be expected that a high sedimentation rate would be obtained, according to Stokes' law.

The applicant has discovered that together with the chemical products, for example polyelectrolytes, it is also necessary to add to the system seed crystals, whose size and specific gravity create a high settling rate and make it possible to coagulate the fine particles according to the principle of orthokinetic coagulation. These auxiliary agents in the form of seeds, which permit a considerable increase in the settling rate of the fine particles, are called in the present description "solid, mineral and granular auxiliary clarification agents (or accelerators)." Although the clarification rate is vastly increased by the simultaneous addition of the usual chemical products and of the auxiliary agents, the optimal result can be obtained only if simultaneously, together with the auxiliary agent, polyelectrolytes are used as chemical products.

It may be conjectured that the molecules of the polyelectrolyte chain on the one hand are bound via the functional groups to the particles that are not easily deposited and are highly dispersed, and on the other hand are bound to the solid, mineral, and granular auxiliary agents added artificially, so that the surface of the materials present in the system may be said to be activated. The rapid progression of this binding process is provoked by the orthokinetic coagulation already mentioned. The solid, mineral, and granular auxiliary agent, which in itself has a fast settling rate, readily collects the fine particles in dispersion which are also activated, which increases the clarification rate of the suspended system. In effect, settling takes place as a function of the settling rate of the agglomerates created by the auxiliary agents added. During settling, the mutual result of the orthokinetic activation generated by the mechanical movement and of the perikinetic activation created by the chemical products is a densification of the turbid liquid, which is characterized by a cross-linked structure.

The solid-materials threshold concentration necessary to produce the cross-linked structure is controlled by the quality of the chemical products (e.g., degree of polymerization of the polyelectrolyte, activity of the functional groups of the polyelectrolyte, etc.), while the time necessary to form the cross-linked structure is determined by the coarseness of the grains and by the quantity and especially the surface qualities of the fine-grained auxiliary agent used for clarification. In a second series of tests, the factors that influenced the efficacy of the auxiliary agent were determined. In these tests, micronized pumice stones were used together with fractions of quartz sand of different coarseness and specific surface. The materials used were sorted with a sieve or, in the classical manner, with hydraulic cyclones. The grain coarseness and the specific properties of the materials are given in the table below:

(see table below)

Product	Coarseness	Approx. specific surface (Lea-Nurse)
	microns	cm ² /g
I. Coarse pumice	30-200	1500
II. Fine pumice	30-100	2000
III. Micro-pumice	15-100	7000
IV. Quartz sand	30-100	220
V. Quartz sand	15-30	500
VI. Quartz sand	0-20	900

The coagulation (or flocculation) agent used was a polymer with a chain structure or a polyelectrolyte with a polymerization degree of 10,000 to 70,000, with a molar cohesion increment of 5-14 K/mol. It is possible, for example, to use the product "Separan NP10" (Dow Chemical) [or] "Sedosan NP10" (which is a copolymer of polyacrylamide and polyacrylic acid, containing 50% water-soluble product). The suspended materials examined consisted of river water with a solid-materials concentration of 300 g/m³ or 50 g/m³ and river sludge with a solid-materials concentration of 1300 g/cm³. The results of the tests conducted are described below:

a. First a polyelectrolyte and a solid and mineral auxiliary agent are added separately and together in identical quantities to the system to be clarified. The results are compared to those that are obtained using aluminum sulfate in a quantity of 60 g/m³. In this series of tests, 10 g/m³ of polyelectrolyte and 2 kg/m³ of auxiliary clarification agent were used. The results obtained are indicated in Table II below. It was deduced that the best results could be obtained by the joint addition of quartz sand IV and polyelectrolyte;

b. The purpose of the other tests was to determine the optimal concentration of the best auxiliary clarification agent and polyelectrolyte necessary for the suspended system under consideration. Tables III and IV contain these guidelines. During testing, it was noted that the optimal clarification effect was produced by the addition of quartz sand IV in quantities of 3-4 kg/m³ and the addition of polyelectrolyte in quantities of 10-20 g/m³ to a static system.

It has been proved by experiments that materials of extensive specific surface with a high adsorption power are unfavorable, since they cannot be used economically in combination with polyelectrolytes for the clarification of highly dispersed suspensoid systems. This proves that the auxiliary clarification agent exercises its action not by adsorption but by formation of a labile bond between the molecules of the polymer with a chain structure and the suspended particles. The round, smooth, and small specific surface of quartz sand is best suited for producing this bond. If, however, it

is desired to replace the quartz sand with an adsorbent of large specific surface, for example pumice stone, it is necessary on the one hand to increase the quantity of the chemical products and, on the other hand, the risk is raised that the efficacy of these chemical products might be virtually eliminated by the specific surface developed because of the fact that all of the functional groups would then be bound.

According to the present invention, quartz sand is thus the best auxiliary clarification agent, since it has a low specific surface, and it must have a grain coarseness of ca. 20 to 100 microns. Its particular advantage lies in the fact that it resists wear and successfully tolerates mechanical stress during regeneration, as a result of which it can be recovered almost without loss in a continuous recovery process.

The implementation of the clarification process in accordance with the invention will be better understood with the aid of the attached drawing and the accompanying Figure 2. Clarification and purification involve the following operations:

1. Sampling of the raw water to be purified;
2. Filtration on a drum (without preliminary decantation);
3. Addition of the chemical products;
4. Clarification with possible regeneration of the auxiliary agent and placement of that agent back in circulation;
5. Filtration on fast filters.

The raw water, which has passed through the filtration drum, is charged with the chemical products necessary for clarification. After adding these products, raw water is led in the direction of arrow *a* through a conduit into cylinder 1 of clarification reactor 3 with a closed bottom. In the meantime, this raw water receives the chemical products as well as the auxiliary agent regenerated in the battery of cyclones 9, with passage through conduit *g*. As part of the purification procedure, the raw water to be purified penetrates the interior cylinder of the clarification reactor after having received all of the auxiliary substances necessary for clarification. It flows from the closed cylinder 1 by spilling over into the pre-clarification space 2, in the shape of a bell jar. After that, it flows at high speed over the lower edge of this bell jar and ascends into the clarification chamber, with gradual reduction of the circulation rate. The clarification agents that have been added to the raw water are disclosed by reduction in the circulation rate and the commencement of settling, and they form a very dense, muddy mass with a cross-linked structure, which is compact and "floating".* After that, the water thus clarified is led into the high-speed filters that are used in the known processes. During the additional purification, it is possible to apply the usual sterilization processes.

**Translator's Note: Not clear what is meant by French "flottant"; normally means "floating" or "flowing" although neither seems appropriate here.*

The turbid, muddy sand that deposits at the bottom of the clarification reactor is led by a continuously-operating dredging device 4 to the bottom 5 of the apparatus. It is then driven by a sludge pump 7 through conduit *c* under a pressure of 2 to 2.5 atm into the battery of hydraulic cyclones 8. This battery classifies the auxiliary agent according to the coarseness of the grains and the specific gravity. In the overflow *f* of the cyclones the water-clarification waste materials are eliminated (i.e., the materials suspended in the river water, metallic hydroxides, etc.), while in the remaining part the sludge-free and purified auxiliary, granular clarification agent which has been activated by the chemical products is recovered. The regenerated auxiliary agent is added to the raw water treated with the chemical products coming from conduit *a* to replace the loss of the auxiliary, granular clarification agent during the operation, the agent is replenished with the help of feed reservoirs 6 containing an agitator, and the replacement supply is gradually introduced via sludge pump 7 into the clarification apparatus while at the same time activating it with the chemical products.

Other specific features of the clarification process in accordance with the invention, the design of which is represented in Figure 2, are drawn from the description of a nonlimiting example presented below, but it is understood that other systems also appropriate to the application of the process may be used as well.

In this clarification operation, 1 m³ of raw water, 30 g of anhydrous aluminum sulfate, 4 g of FeCl₃, and 0.3 g of "Separan NP10" (Dow Chemical) are added. Such a clarification system can handle the purification of 8000 to 10,000 m³ per day. Eight tons of grade IV quartz sand are made to circulate continuously in the 1000 m³-volume reactor. The level of the suspended materials in the raw water is measured with a Pulfrich Nephelometer, wherein the quality of this raw water represents a relative turbidity level of 90-290. The water purified according to the invention has a relative turbidity level of 6-20, with an average of 14; the operating capacity of the clarification is 30,000 to 32,000 m³ per day. The relative turbidity level of the filtered water comes to 2-3.5. The water thus purified has an irreproachable taste and odor and its biological quality is to be considered as greatly improved. The "Alga" index of this purified water is on average comparatively lower than that of the known technique and amounts during the duration of the test to 1/10 of the "Alga" number that could have been expected hitherto. It is possible to further increase the running speed in the clarification system, which makes it possible to considerably reinforce the capacity of this installation.

Compared with the efficacy of the known clarification systems, it should be mentioned that because of the presence of the granular auxiliary agent of a higher specific gravity it is necessary to use a noticeably faster running speed to keep the sludge in suspension during settling than when using the addition of a chemical product. It is possible to increase the efficiency of the clarification system as a

result of this higher running speed. In addition, the use of the granular auxiliary agents produces a substantial increase in the density of the turbid liquid during settling of the sludge and, under the effect of the polyelectrolyte, the particles of these sludges and the suspended materials in the raw water to be purified undergo activation.

By the combined effect of the above-mentioned characteristics, it is possible to obtain a clarification process that is noticeably faster and more intense and also to improve the quality of the purified water.

The industrial tests undertaken by the applicant were conducted in a continuous circulation system, unlike the static system used for the laboratory tests. The continuous circulation system proves to be particularly advantageous for the application of the process according to the invention because the loss of the granular auxiliary agent, which is kept in circulation and regenerated by the battery of hydraulic cyclones, is reduced to a negligible minimum and at the same time the specific quantity of polyelectrolyte used is also lowered. To further enhance the effect of the clarification and to diminish the quantity of polyelectrolyte used, it has been found advantageous to use, simultaneously with the polyelectrolyte, mineral salts containing cations that are bivalent or of an even higher valence and that are routinely used as coagulation agents in the purification of water, e.g., aluminum sulfate and iron chloride or sulfate.

(See tables: I, II, III, and IV)

TABLE I

Modification of the clarification rate and of the solid-materials concentration of purified water as a function of the solid-materials concentration in the raw water used.

Solid materials	Clarification rate, raw water		Solid-materials concentration in the clarified column after 1 hour, raw water			
	Without polyelectrolyte	With polyelectrolyte	Without polyelectrolyte	With polyelectrolyte	With auxiliary agent	With auxiliary agent and polyelectrolyte
g/l	cm/sec	cm/sec	g/l	g/l	g/l	g/l
35	0.0027	0.053	--	--	--	--
23	0.0038	0.18	0.19	0.0	--	--
17.5	0.0046	0.20	0.13	0.0	--	--
14	0.0054	0.20	--	--	--	--
11.5	0.0058	0.29	0.26	0.0	--	--
10.0	0.0060	0.31	0.11	0.0	--	--
6.4	0.0058	0.32	0.18	0.0	--	--
3.3	0.0054	0.48	0.35	0.0	--	--
0.7	Not measurable	Not measurable	0.24	0.09	0.28	0.0
0.35	Opalescent, no clarification		0.14	0.08	0.15	Clear in less than 10'

TABLE II
Clarification by simultaneous addition of auxiliary agent and polyelectrolyte

Addition of polyelectrolyte	g/m ³	Initial concentration of auxiliary agent: 0.36 g/l				
		Addition of auxiliary agent		Solid-materials concentration, time		Observations
			kg/m ³	30 min	60 min	
				g/l	g/l	
Raw sludge				0.34	0.254	After 10 h turbid
Al ₂ (SO ₄) ₃	60			0.36	0.25	"
Separan	10			0.234	0.19	After 2 h clear
Sedosan II	20			0.24	0.19	0
--		Pumice II	2	0.262	0.238	After 10 h turbid
--		Pumice III	2	0.246	0.224	"
--		Quartz sand	2	0.25	0.22	"
Al ₂ (SO ₄) ₃	60	Pumice II	2	0.266	0.246	"
Al ₂ (SO ₄) ₃	60	Pumice III	2	0.33	0.278	"
Al ₂ (SO ₄) ₃	60	Quartz sand IV	2	0.29	0.242	
Separan	10	Pumice II	2	0.214	0.13	After 30 min clear
Separan	10	Pumice III	2	0.158	0.114	"
Separan	10	Quartz sand IV	2	0.134	0.09	"
Sedosan II	20	Quartz sand IV	2	0.142	0.10	"
Al ₂ (SO ₄) ₃	30	Pumice II	2	0.262	0.19	After 10 h turbid
Al ₂ (SO ₄) ₃	30	Pumice III	2	0.27	0.21	"
Al ₂ (SO ₄) ₃	30	Quartz sand IV	2	0.26	0.19	"
Al ₂ (SO ₄) ₃	60	Quartz sand V	2	0.274	0.218	"
Al ₂ (SO ₄) ₃	60	Quartz sand VI	2	0.36	0.33	"
Separan	10	Quartz sand V	4	0.42	0.30	Clear after 5 h
Separan	10	Quartz sand VI	4	0.50	0.38	"

Separan NP10 (Dow Chemical); Sedosan (copolymer of polyacrylamide and polyacrylic acid).

TABLE III
Purification of river water from the Danube (solid-materials concentration 50 g/m³) by simultaneous addition of the auxiliary agent and of the polyelectrolyte.

Chemical products		Auxiliary agent		Observations
Nature	Quantity	Nature	Quantity	
	g/m ³		kg/m ³	
	Raw water			No clarification
Al ₂ (SO ₄) ₃	60	--	--	"
Al ₂ (SO ₄) ₃	60	Pumice III	2	"
Separan	5	Quartz sand IV	1	After 2 h clear
Separan	10	<i>Idem</i>	1	"
Separan	20	<i>Idem</i>	1	"
Separan	5	<i>Idem</i>	2	"
Separan	10	<i>Idem</i>	2	"
Separan	20	<i>Idem</i>	2	"
Sedosan	10	<i>Idem</i>	2	"
Sedosan	20	<i>Idem</i>	2	"
Separan	5	<i>Idem</i>	4	After 20 min
Separan	10	<i>Idem</i>	4	clear
Separan	20	<i>Idem</i>	4	After 10 min
Sedosan	10	<i>Idem</i>	4	clear
Sedosan	20	<i>Idem</i>	4	After 15 min
Separan	10	Pumice III	4	clear
Separan	10	Pumice II	4	After 20 min
Separan	10	Pumice I	4	clear After 15 min clear After 30 min clear After 40 min clear After 1 hour clear

TABLE IV
Clarification of river water (solid-materials concentration 1300 g/m³) by simultaneous addition of the auxiliary agent and of the polyelectrolyte

Polyelectrolyte (Sedosan)	Auxiliary agent (IV quartz sand)	Materials concentration, clarification time			Observations
		2 min	1 hr	3 hr	
g/m ³	kg/m ³	g/l	g/l	g/l	
5	Raw sludge	1.30	0.272	0.19	No clarification
	1	0.196			"
20	1	0.22	0.108	0.08	After 3 h clear
5	2	0.252			After 1 h clear
20	2	0.216			"
5	3	0.188			"
10	3	0.132	0.05	0.02	After 30 min clear
20	3	0.244			"
5	4	0.188			"
10	4	0.116	0.04	0.00	"
20	4	0.08	0.052	0.008	After 15 min clear
5	6	0.36	0.08	0.0	"
10	6	0.272			"
20	6	0.256			After 1 h clear
5	-	0.088			"
10	-	0.20	0.15	0.132	"
20	-	0.216			After 3 h clear

SUMMARY

The present invention has as its object a process for the clarification and purification of surface water and industrial water containing suspended materials, using chemical products, a process characterized by the simultaneous addition to the water to be purified (raw water) of solid auxiliary clarification agents of mineral and granular nature; a polymer with a chain structure forming a polyelectrolyte; and possibly other chemical products routinely used in the purification of water (flocculation agents), and characterized by the recovery after execution of the clarification and filtration operations on the purified water of the solid auxiliary agent of mineral and granular nature, wherein that agent is regenerated and placed back into circulation in the clarification system; this process may also have the following characteristics, considered separately or in combination:

1. As the solid clarification agent of mineral and granular nature, a quartz sand is used with a grain coarseness of 10 to 200 microns and a specific surface of 100-500 cm²/g (according to Lea-Nurse);
2. A polymer whose functional groups have a molar cohesion increment of 5-20 K/mol is used as the polymer with a chain structure forming the polyelectrolyte;
3. A battery of hydraulic cyclones is used for regeneration of the auxiliary, solid and granular clarification agent.

Company name: Nikex Nehézipari Külkereskedelmi Vállalat
 By proxy: Alain Casalonga

N° 1.411.792

Société dite :
Nikex Nehézipari Külkereskedelmi Vállalat

2 planches. - Pl. I

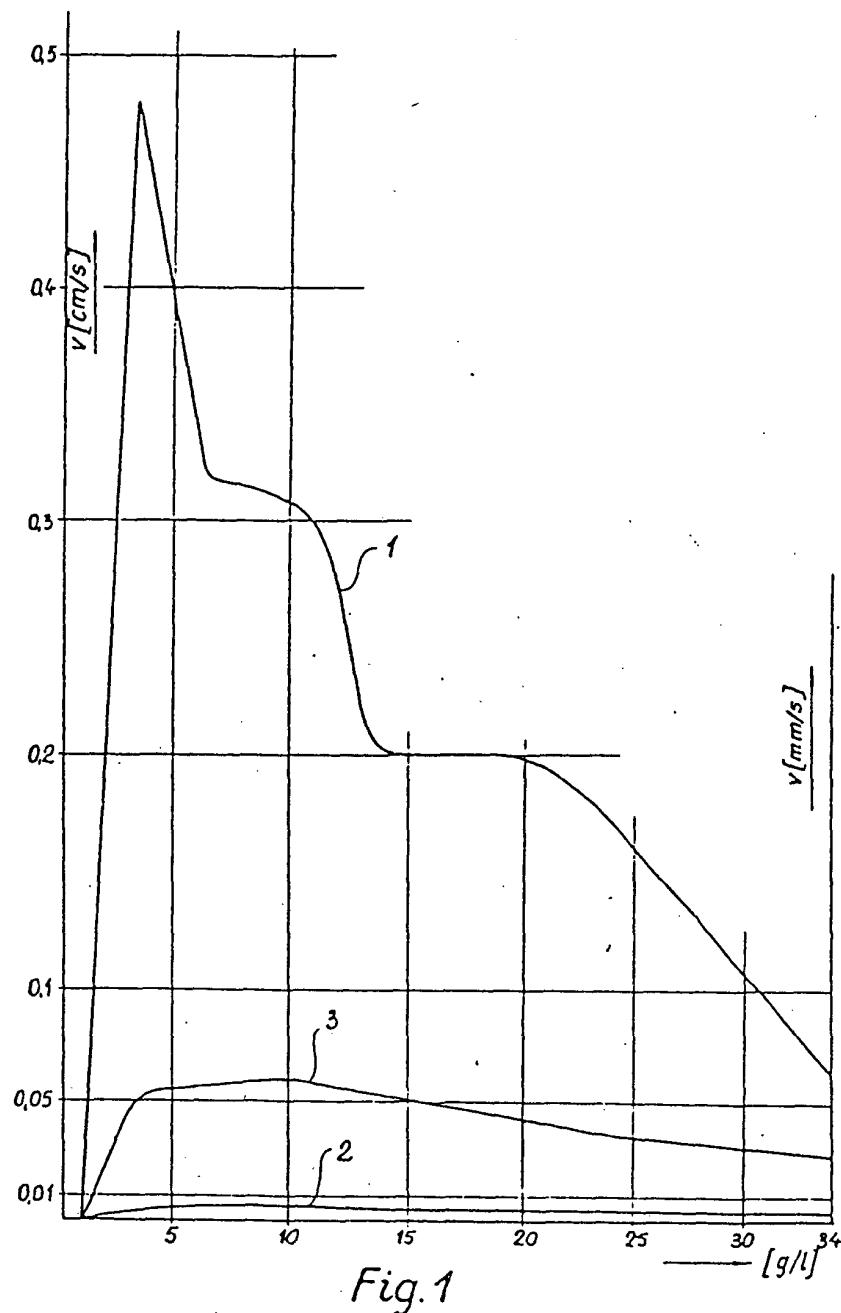


Fig. 1

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2 planches. - Pl. II

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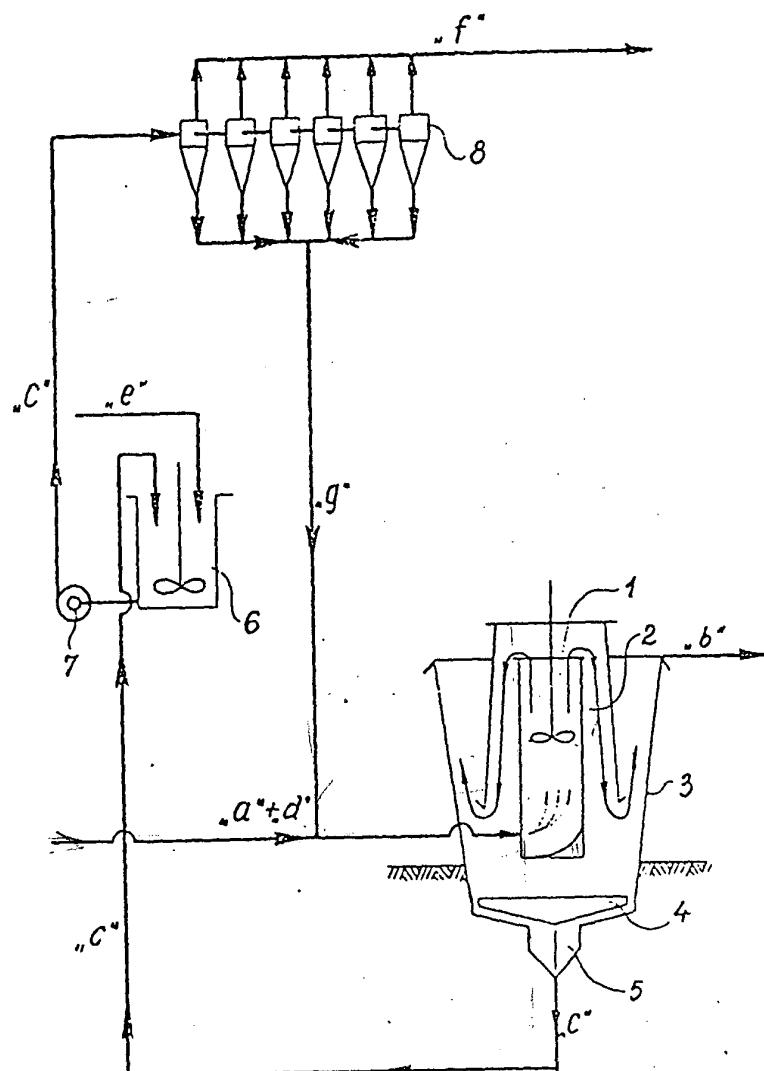


Fig. 2